H/D Exchange Processes Catalyzed by an Iridium-Pincer Complex

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1. Experimental Section

General considerations. All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated by sparging with Ar gas and dried by passage through an activated alumina column.[1] (PNP)IrH_2 (**1**)[2] was prepared according to literature procedures. Other reagents were purchased from commercial vendors, degassed by three freeze-thaw cycles and used without further purification. NMR spectra were recorded on Varian Mercury 300 MHz, 500 MHz or 600 MHz spectrometers (74.5 MHz, 125 MHz and 150 MHz, respectively, for ^{13}C). All NMR spectra were recorded in C_6D_6 or C_6D_{12} and the chemical shifts are reported in ppm relative to the appropriate solvent. High-resolution mass spectra (EI and FAB) were acquired by the California Institute of Technology Mass Spectrometry Facility. The catalytic reactions were monitored by ^1H NMR spectroscopy and the conversions were quantified by integration of the substrate / product signals to an internal standard (a sealed capillary tube containing a standard dioxane solution in C_6D_6 or C_6D_{12}). Mesitylene was used as an internal standard in kinetic experiments. Deuterium incorporation was verified by ^2H and ^{13}C NMR spectroscopies and GC-MS.

Synthesis of [D_2]-1. A solution of (PNP)IrH_2 (**1**, 31 mg, 0.05 mmol) was heated in C_6D_6 in a sealed tube for 1 h at 80 ºC. Removing the volatiles under reduced pressure yielded **[D_2]-1** in a quantitative yield as a red powder. For (PNP)IrD_2: ^1H NMR (300 MHz, C_6D_6) δ 7.83 (dt, J = 8.5, 2.0 Hz, 2H, H_{Ar}), 6.99 (dd, J = 5.8, 4.2 Hz, 2H, H_{Ar}), 6.88 (dd, J = 8.5, 1.8 Hz, 2H, H_{Ar}), 2.21 (s, 6H, CH_3), 2.18-2.03 (m, 4H, CH(CH_3)$_2$), 1.20 (dd, J = 16.3, 7.2 Hz, 12H, CH(CH_3)$_2$), 0.99 (dd, J = 14.6, 7.1 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, C_6D_6) δ 162.10 (s, C_{Ar}), 133.03 (s, C_{Ar}), 131.41 (s, C_{Ar}), 127.85 (t, J = 3.3 Hz, C_{Ar}), 127.48 (t, J = 19.5 Hz, C_{Ar}), 114.80 (t, J = 5.2 Hz, C_{Ar}), 25.05 (t, J = 15.4 Hz,

*C*H(CH$_3$)$_2$), 20.72 (s, CH(*C*H$_3$)$_2$) 19.85 (t, J = 3.3 Hz, CH(*C*H$_3$)$_2$), 18.25 (s, *C*H$_3$). ^{31}P NMR (121 MHz, C$_6$D$_6$) δ 57.7 (s). ^{2}H NMR (300 MHz, C$_6$H$_6$) δ –24.8 (t, J = 10.2 Hz).

Synthesis of (PNP)Ir(py)H$_2$. To a solution of (PNP)IrH$_2$ (**1**, 62 mg, 0.1 mmol in 5 mL pentanes), excess of pyridine (80 mg, 1 mmol in 5 mL pentanes) was added dropwise with stirring. The solution turned yellow and was stirred for an additional 30 min at room temperature. The volatiles were removed under reduced pressure to generate pure (PNP)Ir(py)H$_2$ as a yellow powder. Further recrystallization from pentanes yielded 65 mg of yellow, microcrystalline (PNP)Ir(py)H$_2$ (93%). For (PNP)Ir(py)H$_2$: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 8.81 (d, J = 4.1 Hz, 2H, *H*$_{Ar}$), 8.36-8.19 (m, 2H, *H*$_{Ar}$), 8.12 (dt, J = 8.9, 2.4 Hz, 1H, *H*$_{Ar}$), 6.48-6.19 (m, 6H, *H*$_{Ar}$), 2.23 (s, 6H, C*H*$_3$), 2.11 (m, 2H, C*H*(CH$_3$)$_2$), 1.98 (m, 2H, C*H*(CH$_3$)$_2$), 1.30 (dd, J = 15.9, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (dd, J = 14.7, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (dd, J = 14.5, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.39 (dd, J = 14.1, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), –17.33 (td, J = 13.0, 7.2 Hz, 1H, Ir*H*), –23.39 (td, J = 17.0, 6.8 Hz, 1H, Ir*H*). ^{13}C NMR (74.5 MHz, C$_6$D$_6$) δ 143.5 (s, *C*$_{Ar}$), 137.3 (s, *C*$_{Ar}$), 133.2 (s, *C*$_{Ar}$), 129.7 (s, *C*$_{Ar}$), 129.0 (s, *C*$_{Ar}$), 127.9 (s, *C*$_{Ar}$), 126.3 (s, *C*$_{Ar}$), 126.6 (s, *C*$_{Ar}$), 116.8 (s, *C*$_{Ar}$), 31.3 (t, J = 8.2 Hz, *C*H(CH$_3$)$_2$), 28.6 (t, J = 10.6 Hz, *C*H(CH$_3$)$_2$), 23.1 (t, J = 2.3 Hz, CH(*C*H$_3$)$_2$), 21.4 (t, J = 1.3 Hz, CH(*C*H$_3$)$_2$), 20.9 (t, J = 5.6 Hz, CH(*C*H$_3$)$_2$), 19.5 (t, J = 1.0 Hz, CH(*C*H$_3$)$_2$), 16.1 (s, *C*H$_3$). ^{31}P NMR (121 MHz, C$_6$D$_6$) δ 42.81 (s). Anal. (%) Calcd. for C$_{31}$H$_{47}$IrN$_2$P$_2$: C, 53.05; H, 6.75; N, 3.99. Found: C, 53.21; H, 6.88; N, 3.82.

Control experiments

A mixture of **1** (5 mg, 0.008 mmol) and 1 mL cyclohexane-d_{12} was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 ºC. The reaction was monitored by ^{1}H NMR spectroscopy for 1 week. No hydrogen exchange between the solvent and **1** was observed by NMR.

A mixture of **1** (5 mg, 0.08 mmol), 0.1 mL H$_2$O and 0.9 mL cyclohexane-d_{12} was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 ºC. The reaction was monitored by ^{1}H NMR spectroscopy for 1 week. No hydrogen incorporation in C$_6$D$_{12}$ was observed by NMR or MS.

A mixture of **1** (5 mg, 0.08 mmol), 0.1 mL cyclohexane and 0.9 mL C_6D_6 was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 ºC. The reaction was monitored by ^{1}H NMR spectroscopy for 1 week. No hydrogen incorporation in C_6H_{12} was observed by NMR.

Typical deuteration experiment of aromatic substrates. A mixture of the substrate, catalyst **1** (3.1 mg, 1% mol) and C_6D_6 (1 mL) or D_2O/C_6D_{12} (0.1 mL/0.9 mL) was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 ºC. The reactions were monitored by ^{1}H NMR spectroscopy.

Typical deuteration experiment of tertiary silanes. A mixture of the substrate, catalyst **1** (see Table T1) and 0.8 ml C_6D_6 saturated with D_2O was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 ºC. The reactions were monitored by ^{1}H NMR spectroscopy.

Table T1. Experimental deuteration results.

Substrate (mg/mmol)	Catalyst (mg/mmol)	Solvent (mL)	Time (h)	Product	D (%)
C_6H_6 (39/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	C_6D_6	>95
$C_6H_5CH_3$ (46/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	$C_6H_2D_3CH_3$	>95
o-$C_6H_4(CH_3)_2$ (53/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	*o*-$C_6H_2D_2(CH_3)_2$	>95
m-$C_6H_4(CH_3)_2$ (53/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	*m*-$C_6H_3D(CH_3)_2$	>95
p-$C_6H_4(CH_3)_2$ (53/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	no exchange	n/a
$C_{10}H_8$ (64/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	$C_{10}H_{5.6}D_{2.4}$	40(β); 20(α)
C_4H_4O (34/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	C_4D_4O	92
C_4H_4S (42/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1)	72	C_4D_4S	90
$C_4H_2O(CH_3)_2$ (48/0.5)	3.1/0.005	1 mL C_6D_{12}/D_2O (9:1) or 1 mL C_6D_6	72	$C_4H_{1.7}D_{0.3}O(CH_3)_2$	15
Et_3SiH (58/0.5)	3.1/0.005	0.8 mL C_6D_6/D_2O (sat.)	65	Et_3SiD	>95
Et_3SiH (58/0.5)	3.1/0.005	0.8 mL C_6D_6	65	Et_3SiD	51
Et_3SiH (23.2/0.2)	6.2/0.01	0.8 mL C_6D_6/D_2O (sat.)	20	Et_3SiD	>95
i-Pr_3SiH (32/0.2)	3.1/0.005	0.8 mL C_6D_6/D_2O (sat.)	24	*i*-Pr_3SiD	>95
$(C_6H_5CH_2)_3SiH$ (30/0.1)	3.1/0.005	0.8 mL C_6D_6/D_2O (sat.)	132	$(C_6H_{4.7}D_{0.3}CH_2)_3SiD$	>95
$(Me_3Si)_3SiH$ (25/0.1)	3.1/0.005	0.8 mL C_6D_6/D_2O (sat.)	90	$(Me_3Si)_3SiD$	>90
$PhSiHMe_2$ (34/0.25)	3.1/0.005	0.8 mL C_6D_6/D_2O (sat.)	60	no exchange	N/A
i-$Pr_2SiH(Cl)$ (38/0.25)	3.1/0.005	0.8 mL C_6D_6/D_2O (sat.)	60	no exchange	N/A

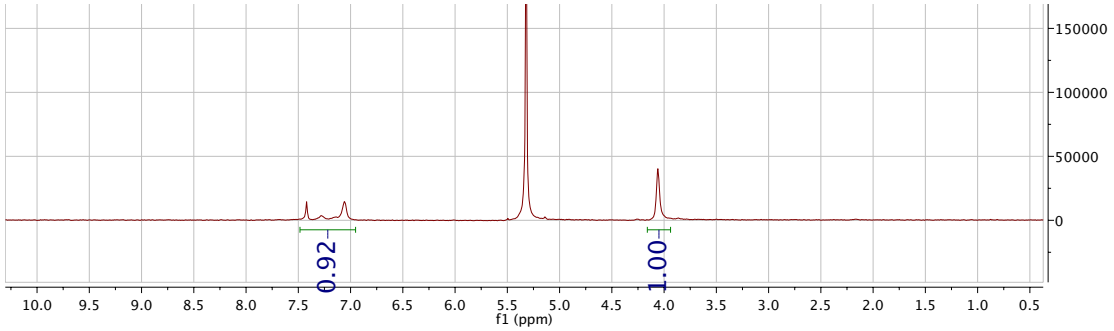

Figure S1. Deuterium NMR spectrum of $(C_6H_4DCH_2)_3SiD$ in CH_2Cl_2 showing competing SiH/D and CH/D exchanges.

Kinetic measurements. A mixture of the substrate, catalyst **1** (3.1 mg, 5% mol), internal standard and C_6D_6 (0.7 mL) was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 ºC. The progress was monitored by ^1H NMR spectroscopy.

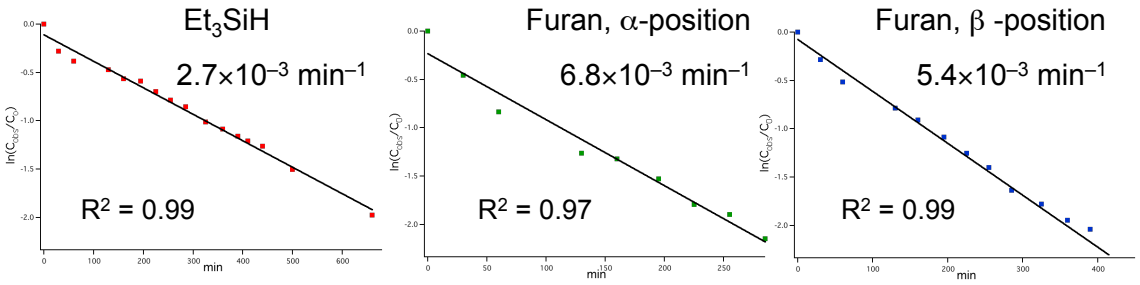

Figure S2. Observed first order plots for deuteration of triethylsilane and furan with 5 mol% of **1** in C_6D_6.

2. References

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(2) Fan, L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 16772.